

stability of such salts. More recently, novel lithium salt compounds such as those set forth in JP-T 2000-60834, too, have been proposed and practically used.

Another possible factor could be the electrochemical
5 stability of solvents used for electrolyte solutions and the content of water in the solvents, and applications of additives and various solvents are now under consideration.

Thus, various methods have been used for high-temperature storage purposes. In consideration of the
10 overall balance of battery properties, however, it is still difficult to improve high-temperature storage properties while keeping other battery properties intact. As an example, this is explained with reference to using LiBF_4 as an electrolyte salt. This LiBF_4 (hereinafter BF
15 for short) is lower in conductivity than but superior in thermal stability to LiPF_6 (PF for short). Accordingly, high-temperature storage properties, for instance, changes in the internal impedance of batteries as detected by the measurement of alternate currents upon storage become
20 lower as compared when PF systems are used. However, low conductivity causes battery capacity to become lower than that of PF system batteries. In other words, when BF is used as an electrolyte salt, it is required to control the composition of an electrolyte solution solvent in view of
25 such considerations and techniques incidental thereto are available as well. Still, the problem that the capacity is lower than that of PF systems remains unsolved.

For recent, more advanced mobile apparatus and instruments for which higher energy densities are needed,
30 it is required to improve the properties of BF systems especially when batteries must have high capacities (when the amount of battery electrode active materials loaded is

increased), in particular keep capacity reductions at low levels.

More recently, batteries housed in flexible aluminum laminated films have been introduced so as to achieve ever
5 higher capacities.

A problem with the aluminum laminated film is that as gases are produced from within a battery after the battery has been assembled, the battery swells. This problem may be surmountable by using γ -butyrolactone for
10 its electrolyte solution as set forth typically in JP-A 2000-236868.

On the other hand, a problem with lithium secondary batteries is that their capacity becomes insufficient at low temperature. Some solutions to this problem are
15 disclosed typically in JP-A's 06-290809 and 08-138738. However, these are chiefly directed to improvements in electrolyte solution compositions; it is still more difficult to improve the low-temperature properties on the premise that γ -butyrolactone should be used for prevention
20 of battery swelling.

SUMMARY OF THE INVENTION

An object of the invention is to prevent the capacity of a battery from decrease when the aforesaid BF
25 salts are used therefor.

Another object of the invention to provide a solution to the problem with the BF system especially when electrodes are designed to have high energy densities.

A more specific object of the invention is to
30 provide a technique by which, when PVDF (polyvinylidene fluoride) is used as an electrode binder, a cyclic carbonate, especially EC (ethylene carbonate) is used as

above, wherein at least the poly(vinylidene fluoride) homopolymer, lactone and lithium fluoroborate-based salt are contained as solid electrolyte components.

(5) The lithium secondary battery according to (3) or (4) above, wherein a lithium-containing composite oxide comprising lithium cobalt oxide and a subordinate component element M, where M is a transition or typical metal element exclusive of Li and Co, in an amount of 0.001 to 2 at% relative to cobalt in the lithium cobalt oxide is contained as a cathode active substance, and 60 to 95% by volume of γ -butyrolactone is contained as an electrolyte solvent.

(6) The lithium secondary battery according to (5) above, wherein said subordinate component element is one or two or more of Ti, Nb, Sn and Mg.

(7) A lithium secondary battery, wherein:
a cathode, an anode and an electrolyte are encased in a housing,
a lithium-containing composite oxide comprising lithium cobalt oxide and a subordinate component element M, where M is a transition or typical metal element exclusive of Li and Co, in an amount of 0.001 to 2 at% relative to cobalt in the lithium cobalt oxide is contained as a cathode active substance,
60 to 95% by volume of γ -butyrolactone is contained as an electrolyte solvent, and
said housing has a thickness of 0.3 mm or smaller.

(8) The lithium secondary battery according to (7) above, wherein said subordinate component element is one or two or more of Ti, Nb, Sn and Mg.

WHAT IS ACHIEVED BY THE INVENTION

First Embodiment

According to the first embodiment of the invention, there is provided an electrode composition containing a lithium fluoroborate-based salt in an electrolyte, wherein
5 a poly(vinylidene fluoride) homopolymer is contained at least as a binder and γ -butyrolactone is contained as an electrolyte solvent. The poly(vinylidene fluoride) homopolymer has been obtained by a emulsion polymerization process.

10 According to the first embodiment of the invention,
there is also provided a lithium secondary battery
comprising the aforesaid electrode composition.

According to the invention, only when this poly(vinylidene fluoride) homopolymer (hereinafter PVDF for short) is used as the binder, the capacity decreases of the fluoroborate lithium-based system (BF system for short) can be reduced. When PVDFs obtained by other synthesis processes are used, such effects are not found at all. Thus, the use of PVDF provides an extremely effective means for making the energy density of the electrode high. Although this mechanism has yet to be clarified, possible explanations could be that active points in PVDF interact with the BF salt in the electrode to reduce resistance, and improvements in the swelling capability due to a crystallinity difference between resins ensure smooth diffusion of lithium with the result that the battery capacity decreases can reduce by half those found so far in the art.

The use of emulsion polymerization processes is disclosed in JP-A 08-250127, etc. According to a typical emulsion polymerization process, a perhaloolefin, i.e., a monomer that provides curing sites, is subjected under

pressure and agitation to emulsion polymerization in the presence of a radical initiator, in substantially the absence of oxygen, and in the presence of an iodine or bromine compound, preferably a diiodine compound in an aqueous medium.

One advantage of the homopolymer obtained by the emulsion polymerization process is that it has very high purity or contains impurities in trace amounts of the order of ppb (parts by billion).

The homopolymer obtained by this emulsion polymerization process has a degree of crystallinity of 30% or higher, especially about 35 to 55%, and a molecular weight of preferably 50,000 or higher, more preferably 100,000 to 140,000.

Preferably for the electrode, a composition comprising an electrode active substance and a binder optionally with a conducting aid is used.

For an anode it is preferable to use an anode active substance such as a carbonaceous material, a lithium metal, a lithium alloy or an oxide material, and for a cathode it is preferable to use a cathode active substance such as an oxide or carbonaceous material capable of intercalating or deintercalating lithium ions. By using such electrodes, a lithium secondary battery having good enough properties can be obtained.

For the carbonaceous material used as the electrode active substance, for instance, an appropriate selection may be made from mesocarbon microbeads (MCMB), natural or man-made graphites, resin-fired carbonaceous materials, carbon blacks and carbon fibers, which are all used in powdery forms. Among others, preference is given to graphite having an average particle diameter of 1 to 30 μm ,

especially 5 to 25 μm . Too small average particle diameters would make charge/discharge cycle life short, and cause capacities to vary largely from battery to battery. Too large average particle diameters would lead to large capacity variations, resulting in an average capacity decrease. Why large capacity variations are caused with large average particle diameters could be due to fluctuations of contact of graphite with a collector or contacts of graphite particles with one another.

For the oxide capable of intercalating and deintercalating lithium ions, preference is given to lithium-containing composite oxides, for instance, LiCoO_2 , LiMn_2O_4 , LiNiO_2 and LiV_2O_4 . Preferably, powders of these oxides should have an average particle diameter of the order of 1 to 40 μm .

If required, conducting aids may be added to the electrode. For instance, graphites, carbon blacks, carbon fibers, and metals such as nickel, aluminum, copper and silver are used, although graphites and carbon blacks are particularly preferred.

Referring to electrode composition, the cathode should preferably have an active substance/conducting aid/binder ratio in the range of 80-94:2-8:2-18 by weight, and the anode should preferably have an active substance/conducting aid/binder ratio in the range of 70-97:0-25:3-10.

For electrode fabrication, the active substance and binder, optionally with the conductive aid, are first dispersed in a binder solution to prepare a coating solution.

Then, this coating solution is coated on a collector. Appropriately but not exclusively, the coating means

should be determined depending on the material and shape of the collector used. In general, various processes such as metal mask printing, electrostatic coating, dip coating, spray coating, roll coating, doctor blade coating, gravure
5 coating and screen printing are used. If required, calendering may subsequently be carried out, using a flat plate press, a calender roll or the like.

The collector used should be appropriately chosen from ordinary collectors depending on the shape of devices
10 for which batteries are used, how to place collectors in cases, etc. In general, aluminum or the like is used for the cathode, and copper, nickel or the like is used for the anode. It is here noted that the collector is usually formed of a metal foil, a metal mesh or the like. While
15 the metal mesh is lower than the metal foil in terms of contact resistance with electrodes, it is understood that low enough contact resistance is obtainable even with the metal foil.

Finally, the solvent is evaporated off to finish up
20 an electrode. The coating thickness should preferably be of the order of 50 to 400 μm .

Lithium Secondary Battery

A lithium battery, whose structure is not critical to the invention, is usually constructed of a cathode, an
25 anode and a separator, and is used in the form of laminated batteries, cylindrical batteries and so on.

The cathode, separator and anode are laminated together in this order, and then compressed together to obtain a battery body.

30 An electrolyte solution to be impregnated in the separate is usually comprised of an electrolyte salt and a solvent. For the electrolyte salt, for instance, lithium

salts such as LiBF_4 , LiPF_6 , LiAsF_6 , LiSO_3CF_3 , LiClO_4 and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ may be used. In the invention, however, lithium fluoroborates such as LiBF_4 are used.

For the solvent for the electrolyte solution, any
5 desired solvent may be used without restriction, provided
that it should have favorable compatibility with
electrolyte salts. Preferable for lithium batteries, etc.,
however, are polar organic solvents that do not decompose
even at high operating voltages, for instance, carbonates
10 such as ethylene carbonate (abbreviated as EC), propylene
carbonate (PC), butylenes carbonate, dimethyl carbonate
(DMC), diethyl carbonate and ethylmethyl carbonate, cyclic
ethers such as tetrahydrofuran (THF) and 2-
methyltetrahydrofuran, cyclic ethers such as 1,3-dioxolane,
15 4-methyldioxolane, lactones such as γ -butyrolactone and
sulforanes.

According to the invention, the solvent for the electrolyte solution should contain at least a lactone such as γ -butyrolactone. This lactone such as γ -butyrolactone should preferably be used in combination with the aforesaid solvents, especially the cyclic carbonate such as EC. The volume ratio between the cyclic carbonate and the lactone should preferably be in the range of 3/7 to 1/9, especially 1/3 to 3/17, as calculated on an ethylene carbonate-to- γ -butyrolactone basis.

In the case where the electrolyte solution is made up of a solvent and an electrolyte salt, the concentration of the electrolyte salt should preferably be in the range of 0.3 to 5 mol/l. Usually at around 0.8 to 2.5 mol/l, the highest ion conductivity is found.

A solid electrolyte or separator sheet that forms the separator should preferably be formed of the aforesaid

poly(vinylidene fluoride) homopolymer, especially one produced by the emulsion polymerization process.

A microporous film for the solid electrolyte used herein should preferably be formed by the following wet
5 phase separation process.

In this wet phase separation process, a film is formed by solution casting while phase separation takes place in a solution. To be specific, a polymer providing a microporous film is dissolved in a solvent capable of
10 solubilizing this polymer, and the resulting film-formation solution is then uniformly coated on a support such as a metal or plastic film to form a film thereon. After this, the film-formation solution cast in a film form is introduced into a solution called a solidifying
15 bath, wherein a microporous film is obtained through phase separation. Alternatively, the film-formation solution may be coated in the solidifying bath.

To improve the adhesion between the aforesaid microporous film and the electrode, adhesives may be used.
20 For instance, polyolefinic adhesives such as Unistall (Mitsui Chemical Industries, Ltd.), SBR (Nippon Zeon Co., Ltd.), Aquatex (Chuo Rika Co., Ltd.) and Adcoat (Morton Co., Ltd.) are usable, although Aquatex or the like is most preferred.

25 The bonding agent is dissolved or dispersed in water or an organic solvent such as toluene, and the resulting solution or dispersion is deposited and fixed onto the microporous film by spreading, coating or the like.

The microporous film should have a porosity of 50%
30 or higher, preferably 50 to 90%, more preferably 70 to 80% and a pore diameter in the range of 0.02 μm to 2 μm , preferably 0.02 μm to 1 μm , more preferably 0.04 μm to 0.8

µm, even more preferably 0.1 µm to 0.8 µm, and most preferably 0.1 µm to 0.6 µm. The microporous film should have a thickness of preferably 20 to 80 µm, and more preferably 25 to 45 µm.

- 5 The microporous film should preferably be formed of a material having a melting point of preferably 150°C or higher, especially 160 to 170°C and a heat of melting of preferably 30 J/g or greater, especially 40 to 60 J/g.

For the separator, still other gelled polymeric
10 materials may also be used. For instance:

- (1) polyalkylene oxides such as polyethylene oxide and polypropylene oxide,
- (2) copolymers of ethylene oxide and acrylates,
- (3) copolymers of ethylene oxide and glycidyl ethers,
- 15 (4) copolymers of ethylene oxide, glycidyl ethers and allylglycidyl ethers,
- (5) polyacrylates,
- (6) polyacrylonitriles,
- (7) fluoropolymers such as polyvinylidene fluoride,
- 20 vinylidene fluoride-hexafluoropropylene copolymers, vinylidene fluoride-ethylene chloride trifluoride copolymers, vinylidene fluoride-hexafluoropropylene fluororubber, and vinylidene fluoride-tetrafluoroethylene-hexapropylene fluororubber.

- 25 The gelled polymer may be mixed with the electrolyte solution or coated on the separator. Moreover, if an initiator is used, the gelled polymer may be crosslinked together by means of ultraviolet rays, EB, heat or the like.

- 30 The solid electrolyte should preferably have a thickness of 5 to 100 µm, preferably 5 to 60 µm, and especially 10 to 40 µm. The solid electrolyte according

to the invention has so high strength that it can have a small thickness. The solid electrolyte according to the invention can be made thinner than a conventional gel electrolyte that cannot practically have a thickness of 60
5 μm or below, and than a separator (of usually 25 mm in thickness) used with a solution type lithium ion battery. It is thus possible to achieve a thin yet large-area battery, i.e., a sheet form of battery that is one advantage of using the solid electrolyte.

10 Further, the separator may be formed of one or two or more of polyolefins such as polyethylene and polypropylene (when two or more are used, the film is of a multilayered structure), polyesters such as polyethylene terephthalate, thermoplastic fluororesins such as
15 ethylene-tetrafluoroethylene copolymers, and celluloses. Furthermore, microporous films, woven fabrics and unwoven fabrics may be used, which have an air permeability of the order of 5 to 2,000 seconds/100 cc as measured according to the JIS-P8117 method and a thickness of the order of 5
20 to 100 μm .

A housing bag is formed of a laminated film in which heat-adhesive resin layers of polyolefinic resins such as polypropylene and polyethylene or heat-resistant polyester resin layers are laminated on both surfaces of an aluminum
25 or other metal layer. The housing bag is formed with one side kept open by thermally bonding two laminated films together in such a way that heat-adhesive resin layers at the end faces of three sides thereof are thermally bonded together, thereby forming a first sealing portion.
30 Alternatively, one laminated film is folded back so that the end faces of both sides are thermally bonded together to form a seal.

To ensure insulation between the metal foil forming the laminated film and a leading terminal, it is preferable to use a laminated film having a multilayered structure comprising, in order from its innermost side, a
5 heat-adhesive resin layer/polyester resin layer/metal foil/polyester resin layer. By use of such a laminated film, it is possible to ensure a certain distance and so insulation between the leading terminal and the metal foil in the housing bag, because the high-melting polyester
10 resin layer remains unfused during heat-bonding. Accordingly, the polyester resin layer in the laminated film should preferably have a thickness of the order of 5 to 100 μm .

Second Embodiment

15 According to the second embodiment of the invention, there is provided a lithium secondary battery comprising a housing with a cathode, an anode and an electrolyte encased therein, wherein a cathode active substance contains a lithium-containing composite oxide comprising
20 lithium cobalt oxide and a subordinate component element M, where M represents a transition or typical metal exclusive of Li and Co, in an amount of 0.001 to 2 at% relative to cobalt in the lithium cobalt oxide and a solvent for an electrolyte contains 60 to 95% by volume of γ -
25 butyrolactone, said housing having a thickness of 0.3 mm or smaller.

With this embodiment, it is possible to provide a lithium secondary battery having satisfactory low-temperature properties with no outgassing even at high
30 temperature. Even when a thin film form of housing is used, any swelling of the housing can be prevented.

In the lithium secondary battery according to the

substituted by two or more thereof. When two or more elements are used, they may be used in any desired combinations with the proviso that Co is substituted within the aforesaid total amount of substitution.

5 Usually, the anode comprises a carbonaceous material, a conducting aid and a binder. The conducting aid is the same as in the first embodiment.

 The carbonaceous material used herein, for instance, includes man-made graphite, natural graphite, pyrolytic
10 carbon, cokes, fired resins, mesophase spheres and mesophase pitch.

 The binder used herein, for instance, include styrene-butadiene latex (SBR), carboxymethyl cellulose (CMC), polytetrafluoroethylene (PTFE), polyvinylidene
15 fluoride (PVDF), ethylene-propylene-diene copolymers (EPDM), nitrile-butadiene rubber (NBR), vinylidene fluoride-hexafluoropropylene copolymers, vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene
terpolymers, polytrifluoroethylene (PTrFE), vinylidene
20 fluoride-trifluoroethylene copolymers, and vinylidene fluoride-tetrafluoroethylene copolymers.

 Electrode production is the same as in the aforesaid first embodiment.

 In the second embodiment, the non-aqueous
25 electrolyte solution has a composition wherein an electrolyte is dissolved in a non-aqueous solvent comprising a mixed solvent that contains as a main component 60 to 95% by volume, preferably 70 to 90% by volume, especially 75 to 85% by volume of γ -butyrolactone
30 (abbreviated as γ -BL) in a solvent component and further contains at least a solvent selected from a chain carbonate, a cyclic carbonate, a chain ester, etc. When

battery is stored in a full-charged state at high temperature, the cathode reacts with the electrolyte to produce gases.

For this reason, a small thin battery has the
5 demerit of being unable to use any active substance of higher performance. As compared with dimethyl carbonate (DMC), methylethyl carbonate (MEC) and diethyl carbonate (DEC) often used with lithium secondary batteries usually encased in housing cans, the γ -butyrolactone used herein
10 is less susceptible to oxidation and outgassing during high-temperature storage in a full-charged state. It is thus possible to use an active substance of higher performance even for batteries comprising housings formed of films that are thinner and softer than housing can
15 materials that are relatively hard and less susceptible to deformation and, hence, fabricate small-sized yet high-performance batteries.

The second embodiment of the invention produces excellent effects even when applied by itself to a lithium
20 secondary battery. It is understood, however, that this embodiment may be combined with the aforesaid first embodiment with synergistic effects which would enable more excellent lithium secondary batteries to be obtained.

25 EXAMPLES

Lithium cobalt oxide, etc. were used for the cathode active substance, and graphite-based materials for the anode active substance. Materials obtained by the carbonization of organic materials, too, may be used for
30 the anode although their properties are different than those of the graphite materials.

Example A-1

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Lithium cobalt oxide was used as the electrode active substance. For electrode preparation, various processes such as those mentioned above may be used. In this case, the following PVDF polymer was used as the binder.

PVDF Elf-Atochem Co., Ltd. (Atofina Co., Ltd.) Kynar 741

This PVDF was prepared by the emulsion polymerization process. With this binder, the electrode was prepared. In this example, a gelled solid electrolyte was used as the electrolyte. This gelled solid electrolyte was synthesized and prepared according to the process set forth in JP-A 11-276298.

More specifically, LiCoO_2 was used as the cathode active substance, acetylene black as the conducting aid, and PVDF Kynar 741 as the binder.

These feeds were weighed in such a way as to give a ratio of LiCoO_2 :acetylene black:PVDF = 83:6:11 by mass. Then, acetone was added in such a way as to give a ratio of acetone:PVDF = 9:1 by mass. These were mixed together at room temperature to obtain a cathode slurry.

On the other hand, mesocarbon microbeads (MCMB) were used as the anode active substance, and acetylene black as the conducting aid.

These feeds were weighed in such a way as to give a ratio of MCMB:acetylene black:PVDF = 85:3:12 by mass. Then, acetone was added in such a way as to give a ratio of acetone:PVDF = 9:1 by mass. These were mixed together at room temperature to obtain an anode slurry.

The thus obtained cathode and anode slurries were each coated by a doctor blade process on a PET film, and the acetone was then evaporated off at room temperature to obtain a sheet.

The following materials were used to prepare a microporous film for the electrolyte film, which was then used to obtain a solid electrolyte.

Twenty (20) parts by weight of polyvinylidene fluoride (Kynar 761 made by Elf·Atochem Co., Ltd.) were dissolved in a mixed solution comprising 40 parts by weight of dimethylacetamide and 40 parts by weight of dioxane, and the resulting solution was then cast by a doctor blade process on a glass sheet at a thickness of 200 μm .

Immediately after the casting, the glass sheet was dipped in a solidifying bath comprising 80 parts by weight of dioxane and 20 parts by weight of water for 10 minutes for solidification, following which the glass sheet was washed in a water stream for 30 minutes, and then dried at 60°C for 1 hour, thereby obtaining a microporous film having a thickness of 50 μm and comprising a poly(vinylidene fluoride) homopolymer.

The thus obtained microporous film was found to have a porosity of 70% and a pore diameter of 0.2 μm .

To give adhesion to the surface of the aforesaid microporous film, it is acceptable to deposit a polyolefinic material thereon by spraying or the like.

The solid electrolyte, cathode and anode were each cut to given size, and the resultant sheets were heat-laminated together at 130 to 160°C. Then, an aluminum grid with a conductive adhesive coated ahead thereon as a collector was heat-laminated on the cathode while a copper grid with a conductive adhesive coated ahead thereof as a collector was heat-laminated on the anode.

Subsequently, the battery assembly was impregnated with an electrolyte comprising 1M $\text{LiBF}_4/\text{EC} + \gamma$ -

butyrolactone (EC:γ-butyrolactone = 2:8 by volume), and then sealed in an aluminum laminated pack to obtain a lithium secondary battery.

The thus assembled battery was measured for its post-charging capacity on the basis of the capacity of a previously fabricated PF system battery. This PF system battery was the same as disclosed with reference to the BF system battery in Example A-1 except the following point.

Electrolyte solution composition EC:DEC = 3:7

10 Comparative Example A-1

In this comparative example, PVDF KF1000 was used for the binder. This was prepared by suspension polymerization. Otherwise, Example A-1 was followed. By the same process as in Example A-1, a battery was fabricated and measured for its capacity.

Example A-2

A battery was obtained in the same manner as in Example A-1 with the exception that the electrolyte solution composition was changed to EC:γ-butyrolactone = 7:2.

Comparative Example A-2

In this comparative example, a battery was obtained in the same manner as in Example A-1 with the exception that the electrolyte solution composition was changed to EC:DEC = 3:7.

The results of these examples were summarized in Table 1. The rate of capacity decreases shown in Table 1 provides an indication of to what degree the initial capacity decreases from the reference capacity of the PF system battery.

Table 1

	Sample	Rate of Capacity Decrease (%)
5	Example 1	4.5
	Example 2	6.7
	Comp. Ex. 1	12
	Comp. Ex. 2	14

As can be seen from Table 1, Examples A-1 and A-2 are more reduced than Comp. Examples A-1 and A-2 in terms of the rate of capacity decreases. This is because γ -butyrolactone and PVDF polymer are used as the gelled solid electrolyte-forming elements and the PVDF polymer shown in Example A-1 is used as the electrode binder.

Such effects cannot be obtained with no coexistence of the gelled solid electrolyte-forming elements and the binder. While the batteries using the gelled solid electrolyte were herein assembled, it is understood that the coexistence of the aforesaid PVDF and γ -butyrolactone would also result in the achievement of similar effects in conventional solution type batteries.

Example B-1

A polymer substance PVDF (Kynar 761A made by Elf • Atochem Co., Ltd.), an electrolyte wherein LiBF_4 was dissolved at a concentration of 2M in a solvent comprising ethylene carbonate: γ -butyrolactone = 2:8 by volume and a solvent acetone were mixed together in such a way as to give a polymer substance:electrolyte:solvent ratio = 3:7:20, thereby preparing a first solution.

A cathode active substance $\text{LiCo}_{0.999}\text{Nb}_{0.001}\text{O}_2$ and a conducting aid acetylene black were dispersed in the first solution in such a way as to give a first solution:active

substance:conducting aid = 2:7.5:1.2 by weight, thereby obtaining a cathode slurry.

A second solution was prepared as in the aforesaid first solution with the exception that the polymer substance:electrolyte:solvent ratio was changed to 3:7:5. An anode active substance graphite was dispersed in this second solution in such a way as to give a second solution:active substance ratio = 2:1 by weight, thereby obtaining an anode slurry.

Using the aforesaid first solution, cathode slurry and anode slurry, a group of electrodes comprising a laminate of cathode-gelled solid electrolyte-anode-gelled solid electrolyte-cathode . . . was prepared. This was encased in a sheet form of housing (an aluminum laminated pack having a thickness of 100 μ m), and the housing was sealed up by means of a sealer. Electrode size was 30 mm x 40 mm.

The thus assembled battery was charged and discharged at 25°C and a cutoff of 4.2 to 3.0 V, 1.0 C for the measurement of its capacity, and then measured for its specific capacity at -20°C. After placed in a full-charged state of 4.2 V, the battery was loaded in an oven of 90°C to measure changes in the battery thickness.

Example B-2

25 A battery was assembled as in Example B-1 for
charging and discharging with the exception that the
cathode active substance was changed to $\text{LiCo}_{0.999}\text{Ti}_{0.001}\text{O}_2$.
After placed in a full-charged state, the battery was
loaded in an oven to measure changes in the battery
30 thickness.

Example B-3

A battery was assembled as in Example B-1 for

charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.999}\text{Sn}_{0.001}\text{O}_2$. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-4

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.999}\text{Mg}_{0.001}\text{O}_2$. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-5

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.99999}\text{Nb}_{0.00001}\text{O}_2$. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-6

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.9999}\text{Nb}_{0.0001}\text{O}_2$. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-7

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.99}\text{Nb}_{0.01}\text{O}_2$. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery

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Comparative Example B-2

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.9}\text{Nb}_{0.1}\text{O}_2$. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Comparative Example B-3

A battery was assembled as in Example B-1 for charging and discharging with the exception that the electrolyte solution composition was changed to ethylene carbonate (EC) and γ -butyrolactone at a ratio of 5:5 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

15 Comparative Example B-4

A battery was assembled as in Example B-1 for charging and discharging with the exception that the electrolyte solution composition was changed to γ -butyrolactone = 100 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Comparative Example B-5

A battery was assembled as in Example B-1 for charging and discharging with the exception that the electrolyte solution composition was changed to ethylene carbonate (EC) and diethyl carbonate (DEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

30 Comparative Example B-6

A battery was assembled as in Example B-1 for charging and discharging with the exception that the

electrolyte solution composition was changed to ethylene carbonate (EC) and methylethyl carbonate (MEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Comparative Example B-7

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.999}\text{Ti}_{0.001}\text{O}_2$ and the electrolyte solution composition was changed to ethylene carbonate (EC) and methylethyl carbonate (MEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

15 Comparative Example B-8

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to $\text{LiCo}_{0.999}\text{Sn}_{0.001}\text{O}_2$ and the electrolyte solution composition was changed to ethylene carbonate (EC) and methylethyl carbonate (MEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Comparative Example B-9

25 A battery was assembled as in Example B-1 for
charging and discharging with the exception that the
cathode active substance was changed to $\text{LiCo}_{0.999}\text{Mg}_{0.001}\text{O}_2$ and
the electrolyte solution composition was changed to
ethylene carbonate (EC) and methylethyl carbonate (MEC) at
30 a ratio of 2:8 by volume. After placed in a full-charged
state, the battery was loaded in an oven to measure
changes in the battery thickness.

Table 2

*) deviations from the inventive range[†]) deviations from the allowable range for -20°C specific capacity⁺⁺) deviations from the allowable range for swelling during storage^{x)} deviations from the allowable range for 1C capacity

From the results of Examples B-1 to B-4 and Comparative Examples B-5 to B-9 shown in Table 2, it is found that even with the cathode active substance to which such additive elements as usually give rise to outgassing are added, it is possible to prevent any outgassing by the use of γ -butyrolactone, and batteries of even smaller size can be fabricated by use of a thin housing. It is here noted that the permissible range of thickness changes is within 0.2 mm.

10 From Examples B-1 to B-10 and Comparative Examples B-1 to B-10, it is found that the low-temperature properties can be improved by the additive elements. It is here noted that the acceptable specific capacity at -20°C is at least 10%.

15 From Examples B-1, B-5, B-6 and B-7 and Comparative
Examples B-1, B-2 and B-10, it is appreciated that the
addition of the additive element in an amount exceeding 2
at% causes capacity decreases and so is unsuitable for
high-capacity batteries. In the inventive examples, the
20 allowable 1C capacity is at least 550 mAh. On the other
hand, the addition of the additive element in an amount of
below 0.001 at% brings about specific capacity decreases
at low temperature, offering a problem on low-temperature
operation.

25 From Examples B-1, B-9 and B-10 and Comparative
Examples B-3 and B-4, it is understood that the proper
amount of γ -butyrolactone to be added is in the range of
60 to 95% by volume.

From the foregoing, it is found that the inventive
30 secondary batteries have improved low-temperature
properties with no risk of swelling at high temperature.
Example C-1

